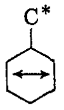
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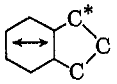
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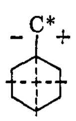
VIII

the axes of polarizability of a mono-substituted benzene. Our data are consistent with the octant rule portrayed in VIII where plus and minus indicate the sign of the ^1L_b Cotton effect due to a strongly interacting group above the plane of the ring. Effects of this nature do not seem to have been considered in detail in the theoretical treatments of the phenyl chromophore.[4f,39] We do not feel qualified, however, to pursue the theoretical analysis beyond this point and hope that it will be taken up by someone else.

(39) D. J. Caldwell and H. Eyring, *Ann. Rev. Phys. Chem.*, **15**, 281 (1964).

The Protonation and Indicator Behavior of Some Ionic Azobenzenes in Aqueous Sulfuric Acid

R. L. Reeves

Contribution from the Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650. *Received December 2, 1965*

Abstract: The effect of ionic solubilizing groups on the indicator behavior of weak organic bases has been examined. The concentration ratios, C_{BH^+}/C_B, and apparent basicities, pK'_{BH^+}, of a number of anionic and zwitterionic *para*-substituted phenylazobenzenes and 2-(*para*-substituted phenylazo)-1-naphthols were measured in 1–80 wt % sulfuric acid. Several monoanionic and all the zwitterionic bases behaved as H_0 indicators, whereas other monoanionic and a dianionic base showed small deviations from this scale. Poorer parallelism was obtained with other acidity function indicators. Apparent pK'_{BH^+} values, based on the H_0 scale, gave excellent correlation with σ_p constants for the phenylazonaphthols and with σ^+ constants in the case of the phenylazobenzenes, with the exception of the *p*-NMe$_2$ derivative. The unprotonated phenylazonaphthols exist almost exclusively as the tautomeric phenylhydrazones in water, whereas the protonated species exist as the resonance-stabilized azonium ions. Monoprotonation of methyl orange gives a mixture of the azonium ion and ammonium ion in which the former is predominant. Monoprotonation of the *p*-NMe$_2$ derivative in the azonaphthol series gives the ammonium ion almost exclusively. Possible reasons for adherence to the H_0 scale and the significance of the apparent pK'_{BH^+} values are discussed.

We were interested in examining the effect of an ionic solubilizing substituent on the activity coefficient ratios of weak organic bases in which the basic center is nonionic. The establishment and evaluation of acidity function scales have to date been largely confined to weak bases where the unprotonated species is a nonionic molecule. The Hammett H_0 scale, as modified by Jorgenson and Hartter,[1] is based on nitrated primary anilines. It has been established that other bases that differ little in structure from the nitrated primary anilines[2] show different indicator properties, and generate their own acidity function scales that vary somewhat from the H_0 scale. Other weak bases whose indicator behavior has been examined include tertiary anilines,[2] aliphatic ethers,[3] amides,[4,5] azobenzenes,[6] azulenes,[7] arylolefins,[8] indoles,[9] phenols[10] and phenolic ethers,[10,11] pyrroles,[12] and uracils.[13] In each case, the indicator properties did not paralle those of the nitrated anilines used to fix the H_0 scale, as indicated by slopes, d log $(C_{BH^+}/C_B)/dH_0$, that deviated from unity. Somewhat less work has been done on evaluating acidity function scales for ionic indicators. Michaelis and Granick utilized the successive protonation of 3-aminothiazine and of 3,9-diaminothiazine to define part of a scale in aqueous sulfuric acid that was based on the mono- and dications.[14] Boyd has defined a scale (H_-) based on cyanocarbon acids that are anionic in their basic form.[15] With the latter indicators, the charged center and the basic center are the same. DeLigny and co-workers have measured the pK_a's of 4-aminophenylazobenzene-4′-sulfonic acid and several of its N-substituted derivatives in methanol–water mixtures (pK') and found that the differences, pK' − pK, vary with solvent composition in quite different ways from the differences for uncharged indicators.[16] From this they conclude that H_0 is not a useful measure of acidity for these indicators in aqueous methanol.

We have investigated the indicator behavior of a series of structurally similar ionic azo compounds in aqueous sulfuric acid to determine the extent to which they conform to existing acidity function scales.

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(1) M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.*, **85**, 878 (1963).

(2) E. M. Arnett and G. W. Mach, *ibid.*, **86**, 2674 (1964).

(3) E. M. Arnett and C. Y. Wu, *ibid.*, **84**, 1680 (1962).

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(6) (a) H. H. Jaffé and R. W. Gardner, *J. Am. Chem. Soc.*, **80**, 319 (1958); (b) S. J. Yeh and H. H. Jaffé, *ibid.*, 81, 3340 (1961).

(7) F. A. Long and J. Schulze, *ibid.*, 83, 3340 (1961).

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(9) R. L. Hinman and J. Lang, *Tetrahedron Letters*, 21, 12 (1960).

(10) A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *J. Am. Chem. Soc.*, 84, 4343 (1962).

(11) E. M. Arnett and C. Y. Wu, *ibid.*, 82, 5660 (1960).

(12) Y. Chiang and E. B. Whipple, *ibid.*, 84, 2763 (1963).

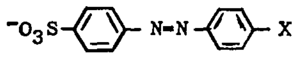
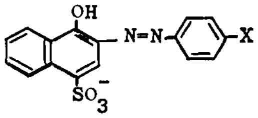
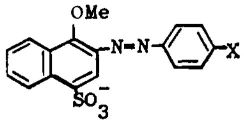
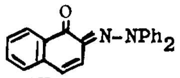
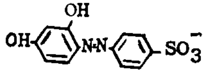
(13) A. R. Katritzky and A. J. Waring, *J. Chem. Soc.*, 1540 (1962).

(14) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **64**, 1861 (1942).

(15) R. H. Boyd, *ibid.*, 83, 4288 (1961).

(16) C. L. DeLigny, H. Loriaux, and A. Ruiter, *Rec. Trav. Chim.*, 80, 725 (1961).

Table I. Spectral Properties of Azo Compounds in Aqueous Solution at 25°

Structure	X	Medium	λ_{max} $(1)^a$ ($\underline{m}\mu$)	$10^{-4}\epsilon(1)$	$\lambda_{max}(2)^b$ ($\underline{m}\mu$)	$10^{-4}\epsilon(2)$
A.						
1	NMe_2	H_2O	463	2.19		
	NMe_2	$0.1\underline{N}$ H_2SO_4	508	4.04	316	0.60
	NMe_2	86.5% H_2SO_4	407^c	3.14		
2	OH	H_2O	350	2.54		
	OH	54.0% H_2SO_4	464^c	5.08		
3	OMe	H_2O	350	2.32		
	OMe	53.0% H_2SO_4	462^c	5.36		
4	H	H_2O	320	2.37		
	H	67.9% H_2SO_4	418^c	3.20		
5	Cl	H_2O	327	2.36		
	Cl	70.6% H_2SO_4	435^c	3.60		
6	NMe_3^+	41.1% H_2SO_4	315	2.49		
	NMe_3^+	79.7% H_2SO_4	408^c	3.23		
B.						
7	NMe_2	H_2O	520	2.21		
	NMe_2	$0.1\underline{N}$ H_2SO_4	485	2.15		
	NMe_2	73.7% H_2SO_4.	518^c	2.49	416^c	1.93
8	OMe	H_2O	508	2.18	372	0.97
	OMe	65.4% H_2SO_4	$565{,}545^{c,d}$	4.0,3.9	445^c	1.1
9	Me	H_2O	497	2.28	365	0.93
	Me	65.4% H_2SO_4	$550{,}524^{c,d}$	3.0,3.2	430	1.3
	Me	96% H_2SO_4	$555, 527^{c,d}$	3.2, 3.4	440	1.14
10	Cl	H_2O	494	2.25	363	0.98
	Cl	77.1% H_2SO_4	$550{,}524^{c,d}$	2.8,3.1	430	1.50
	Cl	96% H_2SO_4	$555{,}528^{c,d}$	3,0,3.3	440	1.30
11	CF_3	H_2O	486	2.08	358	1.00
	CF_3	73.7% H_2SO_4	517^c	2.34	414	1.64
12	SO_3^-	H_2O	490	2.45	362	1.13
	SO_3^-	77.1% H_2SO_4	520^c	2.83	420	2.01
C.						
13	CH_3	H_2O	330	1.35	300	1.43
	CH_3	56.7% H_2SO_4	530,505	2.7,2.7	422	1.19
	CH_3	96% H_2SO_4	537,512	2.6,2.6	430	.88
14	Cl	H_2O	328	1.36	300	1.44
	Cl	96% H_2SO_4	537,512	2.8,3.0	435	1.20
15		10% DMF-H_2O	493	2.07	375	0,48
16		$0.099\underline{N}$ H_2SO_4	383	1.91		
		43.3% H_2SO_4	454^c	3.34		

[a] Absorption maximum at the longest wavelength. [b] Absorption maximum at the second longest wavelength [c] Uncorrected for the medium shift. [d] An unresolved composite band.

The sulfonated *para*-substituted phenylazobenzenes (**1**–**6**) and phenylazonaphthols (**7**–**12**, Table I) seemed well suited for the study because they are very weak bases and differ sufficiently in basicity to permit measurement of concentration ratios, C_{BH^+}/C_B, over a wide range of acidity. They permit the examination of several charge types since they include monoanionic, dianionic, and zwitterionic bases. In addition, the molecular charge is not associated with the entire molecule in the sense of an inorganic ion, or with the basic center, but with a localized hydrophilic group that is somewhat removed from the basic center. No systematic study has been made of this type of ionic indicator in concentrated aqueous acid and we hoped that such a study might provide an indication of the relative importance of net molecular charge to isolated charge in determining the indicator properties of the dyes. We have found that a number of these ionic in-

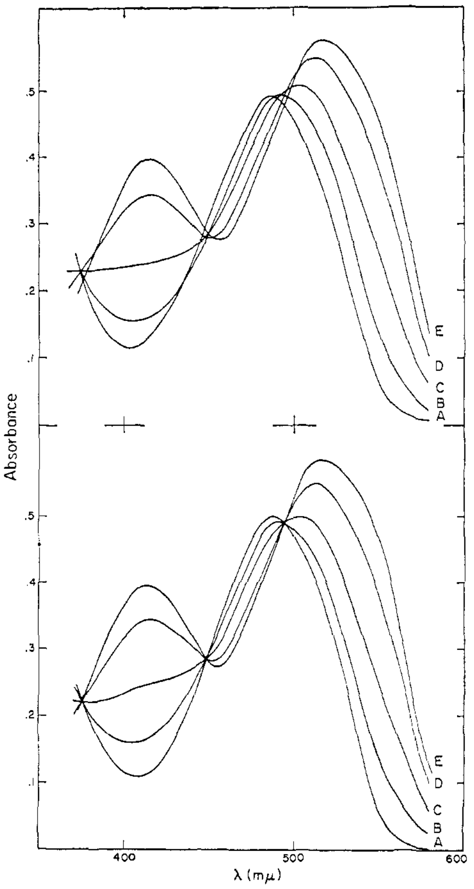


Figure 1. Absorption curves of dye **11** in aqueous sulfuric acid: A, 32.0%; B, 49.0%; C, 54.6%; D, 60.5%; E, 68.6%; upper set, data curves; lower set, curves reconstituted from the "mean" curve and the first vector.

dicators show indicator behavior that parallels that of the nitrated primary anilines, irrespective of charge type.

Results

Analysis of Spectrophotometric Curves. Protonation of the simple phenylazobenzenes gives the usual large bathochromic shift of the long-wavelength band.[17] At sulfuric acid concentrations greater than 40%, a medium shift of the absorption curves causes loss of the isosbestic point. A small lateral shift of the superimposed curves restores the isosbestic point so that, for the simple indicators, satisfactory C_{BH^+}/C_B ratios could be obtained from the shifted curves at a single wavelength.

Protonation of the phenylazonaphthols causes more complex changes in the spectra from which the effect of the medium could not be removed by a simple lateral shift. The curves of compound **11** shown in Figure 1 are typical of all of the phenylazonaphthols. The effect of changing medium did not appear to be the same throughout the entire spectral region examined. A lateral shift of the curves to improve one of the three isosbestic points failed to improve the other two. In addition, the bathochromic shift in the long-wavelength band is not as pronounced as it is for the simple azobenzenes, so that distortion from the medium shift becomes relatively more important. Indicator ratios of sufficient accuracy for our purpose could not be obtained by any subjective manipulation of the curves.

We were able to separate the medium effect from the larger change due to the protonation by analysis of the curves using characteristic vectors. The general application of this method for treating multivariate optical response data has been described.[18] The method can be used empirically for estimating the number of independent factors contributing to the total variation observed in a family of spectrophotometric curves.[19] Briefly, for each acidity, absorptivities, A_i, taken at r wavelengths ($i = 1$ to r), constitute a one-row r-column data vector. For n acidities, the n vectors can be arrayed to form an n-row, r-column data matrix. Description of multivariate response data in terms of characteristic vectors involves the determination of linear transformations of the data to an intrinsic minimum number of parameters containing all the information in the original data. The procedure involves calculation of the variance–covariance matrix from the original n by r data matrix of absorbance vectors.

The characteristic vectors, V_i, are uniquely determined for one family of curves and apply to all the data vectors. When the characteristic vectors are added in proper amounts to some base vector, which we have taken as a "mean absorption curve," $\bar{A}_i$, any of the original curves can be reproduced. The Y's are

$$A_i = \bar{A}_i + Y_1V_{1,i} + Y_2V_{2,i} \ldots + Y_pV_{p,i}$$
$$p \leq r - 1$$

scalar multiples which give the amount of each characteristic vector to be added to the base vector to reproduce a data vector. These will be different for each absorption curve in the family. In the discussion that follows, V_1 will be referred to as the first vector, V_2 as the second, etc. The vectors are orthogonal and represent statistically independent types of variability. The power of the method lies in the fact that, empirically, the number of vectors that must be added to the base vector to reproduce the data vector equals the known sources of variability. In this respect, the method is similar to other matrix methods for the analysis of spectrophotometric curves, where the rank of the matrix is related to the number of independent absorbing species in the system.[20,21] In the present case, the known sources of variability are the protonation equilibrium and the medium effect. The method by which the vectors are derived ensures that the first vector accounts for the largest amount of variability, the second vector accounts for the second largest amount, etc.

Application of the method to data where the medium shift appeared to be unimportant invariably required only one vector in addition to the base vector for a complete reproduction of the data curves. In those cases where the medium shift appeared to be important, two vectors plus the base vector were always required. In several early analyses, the residuals remaining after the second vectors exceeded the known error for the spectrophotometry. This was traced to a small amount of bleaching of the dyes by impurities in

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(17) H. H. Jaffé, S. J. Yeh, and R. W. Gardner, *J. Mol. Spectry.*, **2**, 120 (1958).

(18) J. L. Simonds, *J. Opt. Soc. Am.*, **53**, 968 (1963), and references cited therein.

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(20) S. Ainsworth, *J. Phys. Chem.*, **65**, 1968 (1961); **67**, 1613 (1963).

(21) D. Katakis, *Anal. Chem.*, **37**, 876 (1965).

the acid. Subsequent experiments with pure acid always reduced the residuals remaining after the second vector to within the limits of experimental error. The first vector always accounted for 96% or more of the total variability. The second vector was usually larger in those cases where concentrated acid solutions were required to measure the C_{BH^+}/C_B ratios, indicating that the second vector could be associated largely with a medium effect on the spectra. Thus, analysis of the spectral change accompanying the second protonation of methyl orange in 59–87% sulfuric acid required a second vector that embraced 3.7% of the total variability. On the other hand, protonation of **2** in 10–50% acid required a second vector that hardly exceeded the limits of experimental error (0.06% of the total variability). In those cases where the medium shift is negligible, the numerical analysis offers little advantage beyond the fact that the entire absorption curve is used in determining C_{BH^+}/C_B ratios.

In our treatment we assume, as a first approximation, that the large first vector can be associated wholly with the spectral change accompanying protonation, whereas the small second vector reflects only the medium effect on the spectra. On this assumption, the reconstituted absorption curves obtained by addition of the first vector alone to the base vector will give a family of curves that reflect the acid–base equilibrium, unperturbed by the medium effect. Reconstitution of the curves of **7–12** produced families of curves having three excellent isosbestic points. Figure 1 shows a comparison of the data curves (upper set) with the reconstituted curves (lower set). Although there appears to be no theoretical justification for assigning the derived vectors to known chemical or physical effects, the method appears to be a powerful empirical tool for separating sources of known variability where one source is much larger than others.

Plots of the Y_1 scalar multiples against H_0 produce S-shaped neutralization curves (Figure 2). The same H_0 value for half-neutralization is obtained from a plot of Y_1 or of absorbance (from shifted curves) in the case of each of the azobenzenes **1–6**. Indicator ratios were therefore determined in the usual way by using $C_{BH^+}/C_B = (Y_B - Y)/(Y_{BH^+} - Y)$, where Y_B and Y_{BH^+} are the Y_1 scalar multiples belonging to absorption curves obtained at acidities at which only the basic form or the protonated form, respectively, contributes to the observed spectra, and the Y scalar multiples belong to spectra obtained at intermediate acidities.

With most of the compounds studied, the absorption curves became essentially constant after complete protonation, so that the curve measured at H_0 values equal to $pK'_{BH^+} - 2$ could be taken as the curve of the conjugate acid. This was not the case, however, with the solutions of compounds **8** and **9**. The absorptivities of these solutions continued to change with increasing acidity beyond $pK'_{BH^+} - 2$, so that use of the absorption curve taken at this acidity as a measure of the curve for the conjugate acid resulted in curvature of the plots of log (C_{BH^+}/C_B) against H_0. The neutralization curve of **8** is shown in Figure 2. The method of interpretation is that of Khaldna,[22] by which absorption curves are measured at a number of acidities greater than those needed for complete protonation in order to extend the shoulder of the neutralization curve well beyond the region of curvature to where a linear increase in absorptivity is obtained. It is then assumed that ϵ_{BH^+} is not constant but is a linear function of H_0 throughout the entire region of the neutralization curve and that it varies in the same way at the lower acidities as it does at the acidities above which protonation is complete. The linear shoulder of the neutralization curve (segment AB) is then used to extrapolate ϵ_{BH^+} or the corresponding Y_1 scalar multiple to the acidities at which the C_{BH^+}/C_B ratios are determined (segment BC). The assumption of a linear variation of ϵ_{BH^+} could be tested with solutions of methyl orange (**1**) since the monoprotonated ion exists as the sole ionic species over a very wide region of acidity (Table II). Solutions of **1** did show a small increase in ϵ_{BH^+} over the H_0 range -2 to -4 and this increase was linear. Use of the Y_1 values for BH^+ obtained graphically by this procedure gave linear plots of log (C_{BH^+}/C_B) against H_0 for both **8** and **9**.

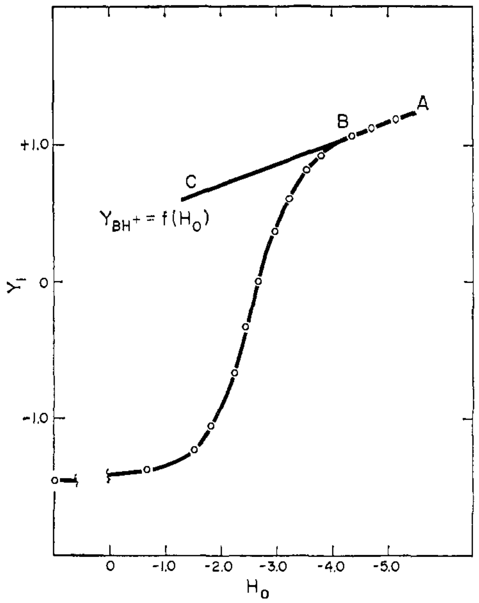

Figure 2. Plot of Y_1 scalar multiple against H_0 for dye **8**.

Apparent Basicities and Applicability of Acidity Function Scales. The bases studied here do not conform perfectly as a series to any existing H_i, but individual members of both structural series adhere either to the H_0 or to the Boyd H_- scale.[15] Table II gives the values of the slopes of log (C_{BH^+}/C_B) plotted against H_0 and against H_- with 95% confidence limits on the slopes. The values of d log $(C_{BH^+}/C_B)/dH_0$ were obtained by least-squares fit of the unweighted data taken within the range pK ± 1.0. The confidence limits were computed from the standard error of the slope and the appropriate Student t factor.[23] The values of d log $(C_{BH^+}/C_B)/dH_-$ were determined graphically. Several of the bases that gave poor conformity to both the H_0 and the H_- scales were also tested against the H_0''' scale of Arnett and Mach, which is based on nitrated tertiary anilines,[2] and against the scale derived by Jaffé for nonionic azobenzenes in 20% ethanol.[6]

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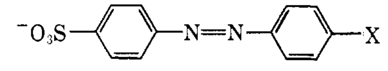
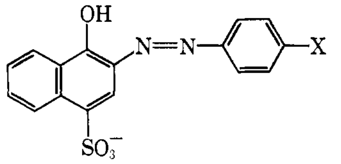
(22) Yu. L. Khaldna in "Reaktsionnaya Sposobnost' Organicheskikh Soedinenii," Vol. 1, No. 2, Tartuskiĭ Gosudarstvennyĭ Universitet, 1964, p 180.

(23) R. L. Anderson and T. A. Bancroft, "Statistical Theory in Research," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, p 156.

Table II. Apparent Basicities of Ionic Azo Compounds in Aqueous Sulfuric Acid at 25°

Structure	X	d log $(C_{BH^+}/C_B)/dH_0$[a]	s_b[b]	n[c]	pK'_{BH^+}	d log $(C_{BH^+}/C_B)/dH_-$
		A. 				
1	NMe_2 NME_2	1.008 ± 0.025 1.041 ± 0.063	0.0078 0.0246	10 7	+3.49 −6.09	1.008 *d*
2	OH	1.171 ± 0.019	0.0088	13	−1.45	0.84
3	OMe	1.142 ± 0.041	0.0166	8	−1.49	0.86
4	H	1.173 ± 0.036	0.0148	8	−3.13	1.12
5	Cl	1.011 ± 0.010	0.0042	9	−3.55	1.06
6	NMe_3^+	0.984 ± 0.078	0.0320	8	−4.95	1.02
		B. 				
7	NMe_2 NMe_2	0.983 ± 0.018 1.006 ± 0.036	0.0077 0.0138	8 7	+3.80 −4.17	 0.98
8	OMe	1.068 ± 0.063	0.0245	7	−2.42	*d*
9	Me	0.984 ± 0.073	0.0296	8	−2.70	0.97
10	Cl	0.867 ± 0.017	0.0072	9	−3.39	0.94
11	CF_3	0.908 ± 0.045	0.0186	8	−3.98	0.98
12	SO_3^-	0.845 ± 0.042	0.0181	9	−3.99	0.90
16		1.107 ± 0.034	0.0149	11	−0.16	

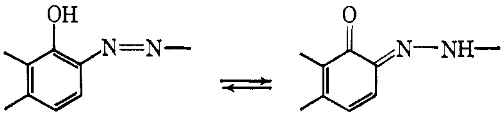
[a] Least-squares slopes of unweighted data, taken within the range pK ± 1.0. The limits of the slopes are for 95 % confidence. [b] Standard error of the slope. [c] Number of log (C_{BH^+}/C_B) values used in determining the slope. [d] Nonlinear plot.

Neither of these latter two scales gave any improvement in the results. For example, the slopes for **3** using the H_0, H_-, and H_0''' scales are 1.17, 0.86, and 0.84, respectively, whereas a nonlinear plot was obtained by using Jaffé's scale.

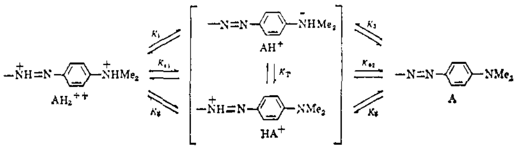
Plots of log (C_{BH^+}/C_B) against per cent acid for most of the azo compounds are as nearly parallel in the region of overlap as similar plots for the H_0 indicators.[24] The apparent failure of some of our indicators to conform perfectly to the H_0 scale in certain acidity regions may reflect some shortcomings of the H_0 indicators in meeting the basic criterion of parallel overlapping log (C_{BH^+}/C_B) plots.[25] It seems significant that the maximum apparent deviations of our indicators from the H_0 scale occur at acidities where drastic changes in the properties and structure of the medium are found.[26]

Because our dyes conform more frequently to the H_0 scale than to the H_- scale, and because the azo nitrogen bears no charge, we have based our experimental pK'_{BH^+} values on the H_0 scale. The derived pK'_{BH^+} values are given in Table II. The two pK'_{BH^+} values given for **1** correspond to pK'_{a1} and pK'_{a2} (eq 1). Throughout, the primed values for the K's indicate that they are relative to the H_0 scale, whereas unprimed constants are thermodynamic constants. The second acid dissociation constants, K_{a2}, for **1** and **7** (monoprotonation) are sufficiently positive to permit measurement of the indicator ratios in very dilute acid where pH can be measured with a glass electrode. These pK'_{BH^+} values correspond closely to values for infinite dilution so that $pK'_{BH^+} \simeq pK_{BH^+}$.

Tautomeric Equilibria. The azo compounds studied here may exhibit two types of tautomerism. (1) The unprotonated phenylazonaphthols exist in solution as equilibrium mixtures of the azo and hydrazone forms.[27] The position of equilibrium is quite sensitive



to the polarity of the solvent, the hydrazone form being the predominant species in polar solvents.[28] (2) The monoprotonated azo compounds possessing *p*-amino groups exist as tautomeric mixtures of the azonium (HA$^+$) and ammonium (AH$^+$) cations.[29] The two experimental acid dissociation constants are defined by



(1)

K_{a1} = ([AH$^+$] + [HA$^+$])[H$^+$]/[AH$_2^{2+}$] and K_{a2} = [A][H$^+$]/([AH$^+$] + [HA$^+$]). The specific acid dissociation constants, K_i, are related to the empirical constants through the tautomeric equilibrium constant, K_T = [HA$^+$]/[AH$^+$]: $K_1 = K_{a1}/(1 + K_T)$; $K_2 = K_{a1}K_T/(1 + K_T)$; $K_3 = K_{a2}(1 + K_T)$; $K_4 = K_{a2}(1/K_T + 1)$.

The unprotonated azo and hydrazone species, as well as the azonium and ammonium ions, exhibit markedly different absorption curves so that the values

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of the tautomeric constants are usually estimated from spectrophotometric measurements. It can be shown that, in general

$$K_T = [A]/[B] = (\epsilon_M - \epsilon_B)/(\epsilon_A - \epsilon_M), \qquad (2)$$

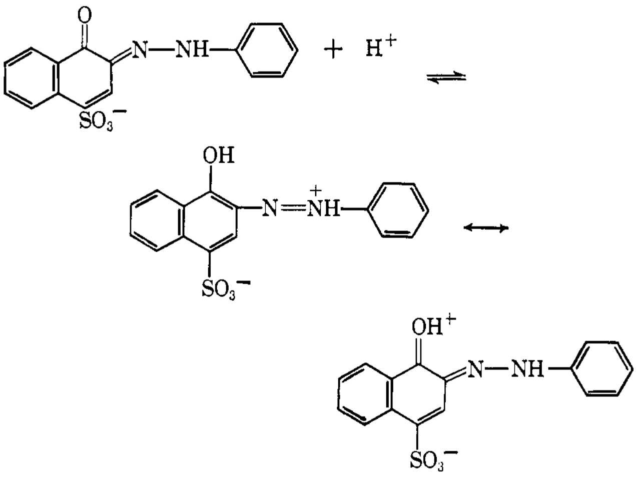
where ϵ_M is the molar absorptivity of the mixture and ϵ_A and ϵ_B are the absorptivities of the individual tautomers. The absorptivities of the pure tautomers cannot be measured directly and are estimated from the spectra of model compounds that exist only in a single form.

Azonium–Ammonium Tautomerism. The spectral properties of the unprotonated and protonated forms of the compounds studied here are given in Table I, along with several derivatives used as model tautomers. The first conjugate acid of methyl orange (**1**) has bands at 508 and 316 mμ; these are assigned to the azonium and ammonium ions, respectively. The value of K_T was calculated by first assuming that $\epsilon_{HA^+} \simeq 0$ at 316 mμ and that ϵ_{AH^+} is equal to ϵ for **6** at 316 mμ in water. These assumptions give a value of 3.2 for K_T. As a second approximation, ϵ_{HA^+} was set equal to 0.2×10^4, a value obtained by Wepster[30] for the first conjugate acid of 4-amino-3,5-di-*t*-butylazobenzene which exists solely as the azonium species. By using this value and the same approximation regarding ϵ_{AH^+}, a value of 4.7 is obtained for K_T. These values of K_T are only slightly larger than those calculated for *p*-dimethylaminoazobenzene by Yeh and Jaffé using similar approximations.[31] The calculated values of pK_1' to pK_4' for this compound are −5.47 (−5.33), −5.97 −6.04), +2.87 (+2.73), and +3.37 (+3.40), respectively. The values in parentheses are based on $K_T = 4.7$, whereas the others correspond to $K_T = 3.2$.

The first conjugate acid of 2-*p*-dimethylaminophenylazo-4-sulfo-1-naphthol (**7**) appears to exist predominantly as the ammonium ion. Monoprotonation shifts the broad band at 520 mμ to shorter wavelengths and gives an absorption curve that is very similar to the spectra of unprotonated analogs having strong electron-withdrawing *para* substituents (**12** and **13**). The characteristic azonium absorption is absent. Thus K_T is small for the conjugate acid of **7**, so that $K_{a1} \simeq K_1$ and $K_{a2} \simeq K_3$.

Azo–Hydrazone Tautomerism. Comparison of the spectra of unprotonated **9** and **10** with their O-methyl derivatives (**13** and **14**) in the 300–600-mμ region shows that neither of the bands exhibited by **9** and **10** in water corresponds to the azo absorption bands of **13** and **14**. We conclude that **9** and **10** exist predominantly as the phenylhydrazones in water, although the spectra do not preclude the presence of small concentrations of the azo tautomer. The similarity of the absorption curve of the diphenylhydrazone (**15**) in 10% DMF–water to the spectra of **8–12** indicates that all of this series exist as hydrazones in water. The fact that the absorptivities of the hydrazone bands of **8–12** are very similar indicates either that the ratio of the two forms is constant for the entire series or that the tautomeric equilibrium constant, $K_T' =$ [hydrazone]/[azo], is large. The value of K_T' is reported to increase markedly with electron-withdrawing X substituents in similar compounds where $0.1 < K_T' < 10$.[32] The fact that the intensity of the strong hydrazone band remains constant with varying X substituents in **8–12** suggests that $K_T' \geq 10$, for each member of the series.

The absorption curves of the protonated phenylazonaphthols show a strong band in the 500–560-mμ region and a weaker one in the 400–450-mμ region. The ratios of the intensities of these two bands change systematically with the nature of the substituent. This suggested that protonation of these substrates produces a tautomeric mixture of monoprotonated species, since a similar change in the ratio of band intensities is observed with monoprotonated derivatives of 4-aminoazobenzene bearing systematically varied substituents.[33] Comparison of the spectra of protonated **9** and **10** with their corresponding protonated O-methyl derivatives showed, however, that the same two bands were present in the ethers (Table I). This indicates that the two bands may be associated with different electronic transitions in a single conjugate acid rather than with single transitions in more than one species. The spectral results also show that the protonated azonaphthols exist as the resonance-stabilized azonium ions, despite the fact that the unprotonated compounds exist predominantly as the phenylhydrazones. The same conclusion was reached by Burawoy and Markowitsch from similar evidence.[34]



Discussion

Although the pK'_{BH^+} values based on H_0 give good measures of relative basicities, the question of how closely the pK'_{BH^+} values approach the thermodynamic values implicit in the use of the H_0 scale still remains. The value of an equilibrium constant lies in its use in calculating concentration ratios outside the narrow concentration range in which they can be measured. If the derived K'_{BH^+} values are not constant outside the range of measurement, the calculated C_{BH^+}/C_B ratios may be in serious error.

The fact that the indicator properties of any base, B, parallel those of an H_0 indicator, A, means only that

$$\mathrm{p}K'_{BH^+} = \mathrm{p}K_{BH^+} + \log\left(\frac{f_A f_{BH^+}}{f_{AH^+} f_B}\right) = \mathrm{p}K_{BH^+} + \text{constant} \qquad (3)$$

If $f_A/f_{AH^+} = f_B/f_{BH^+}$, then p$K'_{BH^+} =$ pK_{BH^+}. The

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(30) A private communication referred to in ref 31.

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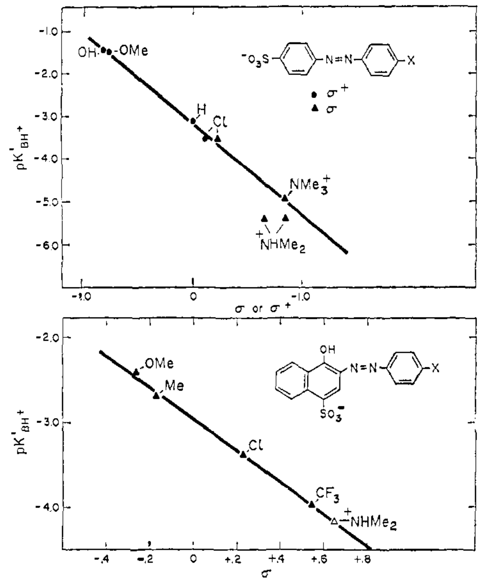


Figure 3. Plots of pK'_{BH^+} against σ or σ^+. Δ,σ value for $NHMe_2^+$ calculated from correlation line determined by solid data points.

parallelism between H_0 and the H_- function[15] and between H_0 and the H_+ function[35] over certain ranges of acidity has been noted.

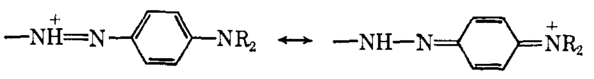
While the degree of solvation of the ionic indicators employed here will certainly be greater than that of the H_0 indicators, this fact may not be important since it is the *difference* in solvation between the indicator species that influences the activity coefficient *ratios*. The solvation of the ionic solubilizing groups will probably be the same in the protonated and unprotonated species. The experimental fact that f_B/f_{BH^+} changes in the same way as f_A/f_{AH^+} with changing medium suggests that the over-all molecular charge due to the presence of ionic solubilizing groups in an indicator may not have a significant effect on the indicator properties compared to similar nonionic indicators. Although the question of whether K'_{BH^+} is equal to K_{BH^+} for those indicators where d log $(C_{BH^+}/C_B)/dH_0 = 1$ cannot be completely answered at this point, the data and our model of the system certainly allow the possibility.

The slope, d log $(C_{BH^+}/C_B)/dH_0$, is 1.107 ± 0.034 for the dihydroxyazobenzene, **16**. The true pK_{BH^+} can be determined for this compound, so an estimate of the magnitude of the difference, $pK_{BH^+} - pK'_{BH^+}$, is available for one of the compounds showing deviation from H_0 behavior. The log (C_{BH^+}/C_B) values for this base can be measured over the concentration range 0.1 to 2 M, where a plot of log (C_{BH^+}/C_B) − log C_{H^+} against C_{H^+} is linear. Extrapolation of such a plot to zero C_{H^+} gives pK_{BH^+} as the intercept, and is −0.48 for this dye. The difference, $pK_{BH^+} - pK'_{BH^+}$, is −0.32, an error that is not too great for many purposes. The difference should be smaller for the compounds displaying more ideal H_0 behavior.

The results in Table II show that the failure of some of the bases to adhere exactly to the H_0 scale is not related to a particular substituent or to a particular charge type. Thus, the methoxy-substituted base conforms in the phenylazonaphthol derivative but not as the azobenzene, whereas the reverse is true with the p-chloro derivatives. All four of these bases are anionic. If any generalization can be made, it is that the bases that are zwitterions (**6**, and monoprotonated **1** and **7**) behave as nonionic bases. This behavior suggests that local charged centers may not affect the indicator behavior as long as the net charge is zero. Considerably more zwitterionic indicators will have to be studied before this observation can be generalized. The separation of charge centers in zwitterionic bases could well affect their behavior.

The fact that some of the bases do not adhere perfectly to the H_0 scale does not introduce large errors in comparing relative basicities on this scale. Figure 3 shows Hammett plots of pK'_{BH^+} against σ or σ^+ for both series. Most of the σ_p constants are based on the ionization of substituted benzoic acids and are known with fairly high precision.[36] These constants were used to fix the correlation lines in the lower figure; other σ_p constants were evaluated from these lines and the corresponding pK'_{BH^+} values. The largest deviation of any pK'_{BH^+} in the azonaphthol series from the correlation line is 0.05 log unit, which is of the magnitude of the combined uncertainties in H_0, log (C_{BH^+}/C_B), and σ_p. The largest deviation in pK'_{BH^+} of the azobenzene series, excluding the two pK'_{BH^+}'s of **1**, is 0.13 log unit. The σ_p constant for p-SO_3^- as calculated from the pK'_{BH^+} of **12** is +0.54, the same as the constant for p-CF_3. This is considerably more positive than the value determined from the pK_a of p-sulfobenzoic acid in water at 25°, but is in good agreement with the value derived from the pK_a's of p-sulfonanilinium and p-sulfophenol.[37] The σ_p value for $NHMe_2^+$, derived from the pK_1' of **7**, is +0.65. The σ_p value for $NHMe_2^+$ is usually set equal to the value for NMe_3^+, which is 0.82 ± 0.2, based on the ionization of benzoic acids. Our σ_p value for $NHMe_2^+$ agrees exactly with the σ_p value for NMe_3^+ based on the ionization of *para*-substituted dimethylanilinium ions in water at 25°.[38] The σ^+ constants for OMe and Cl are those of Brown and Okamoto,[39] and the value for OH is that derived by Deno and Evans from the triarylmethanol–trialkylmethyl cation equilibrium.[40]

Neither pK_4' nor pK_1' for methyl orange (**1**) gives acceptable correlation with the other pK'_{BH^+} values for the azobenzenes if reasonable σ^+ constants for NMe_2 or σ_p constants for $NHMe_2^+$ are used. Figure 3 shows the large deviation for $NHMe_2^+$ when either the σ_p value of +0.65 or +0.82 is used. The point for NMe_2 is not shown in Figure 3, but the deviation amounts to 2.4 log units when the most negative value reported for this substituent (−1.87[40]) is used. In order to obtain a good correlation, a σ^+ value of −3.0 would have to be assigned to NMe_2 for this equilibrium. Although it is recognized that the unusually high basicities of azobenzenes containing *para*-amino groups are due to a large contribution of the quinone diimine structure to the conjugate acid



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we hestitate to assign this σ^+ value on the basis of these data since pK_4 for **1** is very close to the thermodynamic constant and the other p$K'_{\mathrm{BH^+}}$ values may not be.

Experimental Section

The sulfonated azobenzenes **1**, **2**, **4**, and **16** were Eastman grade or Eastman Certified grade products that were recrystallized to constant absorption curves. Compound **3** was prepared from **2**, and **5** was obtained by sulfonation of *p*-chloroazobenzene. The phenylazonaphthols were prepared in the usual way.

The methyl ethers of **9** and **10** (**13** and **14**) were prepared by reaction of the dyes with methyl iodide in DMF containing a small amount of aqueous sodium carbonate. Methyl orange was quaternized by warming the dye with a large excess of methyl iodide in DMF. The very insoluble inner salt precipitated from the reaction medium and was purified by repeated digestions with 50% ethanol on a steam bath. The diphenylhydrazone **15** was prepared by condensation of 1,2-naphthoquinone with 1,1-diphenylhydrazine in aqueous acetic acid, mp 173–175° (lit.[41] mp 171–172°). All compounds except **14** gave elemental analyses within 0.3% of the theoretical for at least two elements.

Baker and Adamson reagent grade sulfuric acid gave the most reproducible results. At the low concentrations of substrates used here (2.5×10^{-6} *M*), trace impurities present in other sources of acid caused partial reduction of the substrates. The acid solutions were prepared by diluting predetermined volumes of concentrated acid, delivered from a buret. Replicate determinations of indicator ratios in solutions prepared by this method gave identical results. The acidity function values, H_i, corresponding to a given acid concentration were obtained from large plots of H_i against weight per cent sulfuric acid. The values of H_0 given by Paul and Long[24] were used up to 60% acid. At higher acidities, the H_0 values determined by Jorgenson and Hartter[1] were used.

The absorption curves were measured on a Cary Model 14 spectrophotometer over a sufficiently wide wavelength range to include the bands characteristic of both the azo and the azonium species. To avoid deviations from Beer's law the concentration of azo compound was 2.5×10^{-6} *M*; 10-cm cuvettes were used for the measurements.

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Phenyldiimide. III. Ferric Ion Catalyzed Formation of Free Radicals in Heterolysis of Azo Compounds[1,2]

Jesse Nicholson and Saul G. Cohen

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts. *Received December 29, 1965*

Abstract: Ferric ion catalyzes effectively the methanolysis of N-phenyl-N′-benzoyldiimide ($C_6H_5N{=}NCOC_6H_5$, I) leading to higher yields of methyl benzoate and phenyldiimide ($C_6H_5N{=}NH$, II) than the acid- or base-catalyzed reactions. The ferric ion oxidizes II efficiently, minimizes its reaction with I, and leads to high yields of phenyl radical from I at room temperature. In methanol the phenyl radical is converted to benzene, in the presence of benzene to biphenyl, in the presence of nitrobenzene to nitrobiphenyls, and in the presence of carbon tetrachloride to chlorobenzene in high yield. Ferric ion catalyzed methanolyses of compound I, of N,N′-dibenzoyldiimide ($C_6H_5CON{=}NCOC_6H_5$, III), and of diethyl azodicarboxylate ($C_2H_5O_2CN{=}NCO_2C_2H_5$, IV) lead to free radicals which add to acrylonitrile and initiate its polymerization more effectively than the acid-catalyzed methanolyses of these azo compounds.

Early attempts to prepare and isolate aryldiimides (Ar—N═N—H) led to nitrogen and the hydrocarbons ArH, and to the conclusion that the diimides were unstable and decomposed to these products.[3] Phenyldiimide ($C_6H_5N{=}NH$) has been suggested as an intermediate in the oxidation of phenylhydrazine; when the oxidation was carried out in water, only benzene and nitrogen were isolated.[4] When ether[5a] or phenylhydrazine[5b] itself was solvent other products were isolated, including biphenyl. Subsequently, oxidation of phenylhydrazine[6] and of pentafluorophenylhydrazine[7] in aromatic solvents led to appropriate biaryls, indicating that phenyl and pentafluorophenyl radicals had been formed by decomposition of or by oxidation of the diimides.

We have recently reported[2] that the thermally stable compounds N-phenyl-N′-carbethoxydiimide ($C_6H_5N{=}NCO_2C_2H_5$) and N-phenyl-N′-benzoyldiimide ($C_6H_5N{=}NCOC_6H_5$, I) undergo rapid acid- or base-catalyzed alcoholysis and lead to free phenyl radicals, presumably *via* phenyldiimide II. Detailed investigations of the parent compound, diimide HN═NH, have been reported in recent years.[8-10] Some spectral observa-

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(1) We are pleased to acknowledge generous support of this work by the National Science Foundation, GP 1833, and predoctoral fellowships under title IV of the National Defense Education Act, and of the National Institutes of Health, GM 24864.

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